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(54) NICKEL HYDROXIDE POWDER FOR ALKALINE BATTERY AND NICKEL HYDROXIDE ELECTRODE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nickel hydroxide electrode including the nickel hydroxide active material for alkaline battery, having an improved utilization factor and improved capacity density.

SOLUTION: This nickel hydroxide electrodes uses an active material obtained by forming a surface of the powder, mainly composed of nickel hydroxide having divalent or higher nickel with a cobalt compound having divalent or higher cobalt. For example, the active material obtained by coating a surface of the oxynickel hydroxide powder with an oxycobalt hydroxide layer is used. This active material is used as a raw material and held by a three-dimensional porous body so as to form an electrode.

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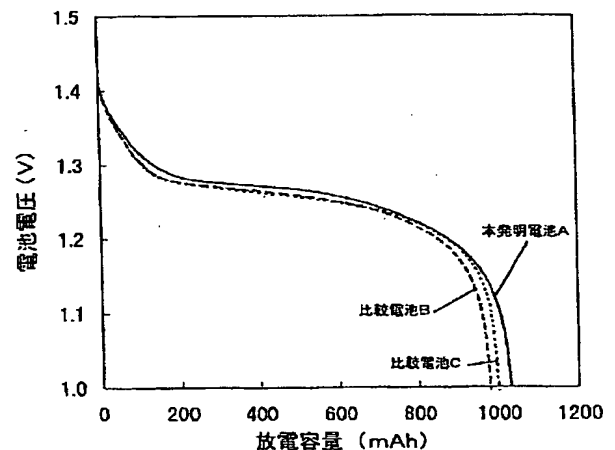
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(54) 【発明の名称】 アルカリ電池用水酸化ニッケル粉末およびこれを用いた水酸化ニッケル電極

(57) 【要約】

【課題】 利用率の改善されたアルカリ電池用水酸化ニッケル活物質と容量密度の改善された水酸化ニッケル電極を提供する。

【解決手段】 ニッケルの価数が2価を越える水酸化ニッケルを主体とする粉末の表面に、コバルトの価数が2価を越えるコバルト化合物が形成されたものを活物質とする。例えば、オキシ水酸化ニッケル粉末の表面がオキシ水酸化コバルト層で覆われたものを活物質とする。そして、これを原料とし、三次元多孔体にこれを保持させることにより電極とする。



【特許請求の範囲】

【請求項 1】 ニッケルの価数が 2 価を超える水酸化ニッケルを主体とする粉末であって、該水酸化ニッケル粉末の表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されていることを特徴とするアルカリ電池用水酸化ニッケル粉末。

【請求項 2】 上記水酸化ニッケル粉末のニッケルの平均価数が、これを被覆する 2 価を超える価数を有するコバルト化合物のコバルトの平均価数を超えないことを特徴とする請求項 1 記載のアルカリ電池用水酸化ニッケル粉末。

【請求項 3】 水酸化ニッケルを主体とする粉末を三次元多孔体に保持してなる水酸化ニッケル電極であって、前記水酸化ニッケルを主体とする粉末が、ニッケルの価数が 2 価を超える水酸化ニッケルを主体とする粉末であって、該水酸化ニッケル粉末の表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されていることを特徴とする水酸化ニッケル電極。

【請求項 4】 表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されたニッケルが 2 価以下の価数を有する水酸化ニッケル粉末と、表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されたニッケルが 2 価を超える価数を有する水酸化ニッケル粉末とが混合されて三次元多孔体に保持されていることを特徴とし、かつ三次元多孔体に保持される水酸化ニッケル粉末全体のニッケル平均価数が、2.07 価以上の価数を有していることを特徴とする水酸化ニッケル電極。

【請求項 5】 上記水酸化ニッケル電極に含有されるニッケルが 2 価を超える価数を有する水酸化ニッケル粉末のニッケルの平均価数が、これを被覆する 2 価を超える価数を有するコバルト化合物のコバルトの平均価数を超えないことを特徴とする請求項 2 または 3 記載の水酸化ニッケル電極。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、アルカリ電池用水酸化ニッケル活物質およびこれを用いた水酸化ニッケル電極に関する。

【0002】

【従来の技術】水酸化ニッケルを主体とする化合物を活物質とする水酸化ニッケル電極は、例えば、ニッケル-カドミウム蓄電池やニッケル-金属水素化合物蓄電池などのアルカリ電池の正極として用いられている。これらのアルカリ蓄電池は小型携帯電子機器の電源として用いられ、その機能向上の手段としてアルカリ蓄電池の高容量化が求められているため、アルカリ蓄電池の放電容量を決定する水酸化ニッケル電極の高エネルギー密度化が不可欠である。

【0003】従来、水酸化ニッケル電極としては、ニッケル粉末を多孔性のパンチングメタル上に焼結させて得

られた基板上に水酸化ニッケル活物質を含浸させて製作される焼結式のものが多く用いられてきた。しかし、焼結式水酸化ニッケル電極は基板の多孔度が概ね 80%と小さく、多量の活物質を充填することが困難であるため、水酸化ニッケル電極の高エネルギー密度化には不利であった。

【0004】一方、基板として三次元金属多孔体である発泡状ニッケルや繊維状ニッケルを用い、これに水酸化ニッケル活物質を保持させた非焼結式の水酸化ニッケル電極は、基板の多孔度が 95%以上と高く、前記焼結式水酸化ニッケル電極と比較して水酸化ニッケル電極の高エネルギー密度化に有利である。このことから、最近のアルカリ蓄電池の高容量化についての研究は、主に非焼結式水酸化ニッケル電極を用いておこなわれている。この非焼結式水酸化ニッケル電極では、水酸化ニッケルの導電性が低いため、導電剤として水酸化コバルト、一酸化コバルト、コバルトサブオキシド等のコバルト化合物や金属コバルトを水酸化ニッケル電極中に混合したり、例えば特開昭 62-117267 号公報に記載されているようにこれらで水酸化ニッケル粒子表面を被覆する方法により添加したりすることが必要となる。

【0005】添加されたこれらコバルト化合物は、化成初充電における電気化学的な酸化によって導電性の高いオキシ水酸化コバルトに変換されて電極内に導電性ネットワークを形成し、水酸化ニッケル電極中で有効な導電剤として作用するものと考えられている。なお、水酸化ニッケル粒子表面を被覆する方法によれば、コバルト化合物を単独で添加した場合よりも、コバルト化合物と水酸化ニッケルとの接触面積が大きく、活物質利用率の向上の効果が大きくなる。

【0006】

【発明が解決しようとする課題】アルカリ蓄電池の水酸化ニッケル電極の活物質である水酸化ニッケルは、充電により酸化されてオキシ水酸化ニッケルとなり、また放電により水酸化ニッケルに還元されるが、この水酸化ニッケルは、オキシ水酸化ニッケルよりも導電性が低い物質である。このため、充電初期、特に化成初充電の充電効率が低いという問題がある。

【0007】そこで、このような問題を解決する為に、例えば、特開平 2-262245 号公報、特開平 2-234356 号公報に記載されているように、水酸化ニッケル電極の製作時にあらかじめ水酸化ニッケルよりも導電性が高い物質であるオキシ水酸化ニッケルを均一に添加しておくという方法が考えられている。しかしながら、上記従来の水酸化コバルトや一酸化コバルト等のコバルトの価数が 2 価以下のコバルト化合物や金属コバルトを添加した水酸化ニッケル電極中にオキシ水酸化ニッケルを添加すると、計算により算出される放電容量に比べてその容量が小さくなることが分かった。

【0008】そこで、本発明者らは、この原因を究明し

た結果、コバルトの価数が 2 価以下のコバルト化合物の一部が、もしくはコバルトの価数が 2 価を超えるものであっても、2 価を超える価数の水酸化ニッケルよりもコバルトの価数が低い場合にはこのコバルト化合物の一部が、酸化力の高いオキシ水酸化ニッケルによって酸化されて高次コバルト化合物となり、水酸化ニッケル電極内においてコバルト化合物の偏在が生じて、水酸化ニッケル電極の導電性を維持するために必要であると考えられているオキシ水酸化コバルトの導電性ネットワークの形成が十分に行われなくなるのではないかという結論に達し、これに基づき予め水酸化ニッケル粒子表面にオキシ水酸化コバルトを形成しておくことによってこの問題を解決することを可能にした。そして、この過程の中で本発明者らは、さらに、放電容量を大きくする方法を見出した。本発明は、このさらに改善されたアルカリ電池用水酸化ニッケル活物質およびこれを用いた水酸化ニッケル電極を提供することを目的とする。

【0009】

【課題を解決するための手段】本発明のアルカリ電池用水酸化ニッケル粉末は、ニッケルの価数が 2 価を超える水酸化ニッケルを主体とする粉末であって、該水酸化ニッケル粉末の表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されていることを特徴とする。

【0010】また、本発明の水酸化ニッケル電極は、水酸化ニッケルを主体とする粉末を三次元多孔体に保持してなる水酸化ニッケル電極であって、前記水酸化ニッケルを主体とする粉末が、ニッケルの価数が 2 価を超える水酸化ニッケルを主体とする粉末であって、該水酸化ニッケル粉末の表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されていることを特徴とする。

【0011】本発明の水酸化ニッケル粉末は、ニッケルの価数が 2 価を超える水酸化ニッケルを主体とするが、その価数が 3 価を超えると、アルカリ蓄電池の充放電サイクル寿命性能に悪影響をおよぼすと考えられているγ-オキシ水酸化ニッケルが生成するため、上記主体となる水酸化ニッケルのニッケルの価数は 3 価以下であることが好ましい。

【0012】また、ニッケルの価数が 2 価を超える水酸化ニッケル粉末の表面に形成されるコバルト化合物は、より好ましくは層状に水酸化ニッケル粉末を覆うように形成されているのが良く、そのコバルトの価数は、水酸化ニッケル粉末のニッケルの価数よりも低い場合、上記水酸化ニッケル粉末の強い酸化力のためにコバルト化合物が酸化されやすく、その導電性を維持することが困難となるため、水酸化ニッケル粉末の価数と同等、もしくはそれ以上であることがより好ましい。すなわち、このコバルト化合物は活物質となる水酸化ニッケル粉末の導電性を担うものの一つであり、高い導電性を有するものであって、水酸化ニッケル粉末のニッケルの平均価数が、これを被覆する 2 価を超える価数を有するコバルト

化合物のコバルトの平均価数を超えないようにするのが良い。

【0013】また、上記三次元多孔体は、発泡状ニッケルや繊維状ニッケル等の三次元金属多孔体であるのが好ましい。

【0014】さらに、本発明の水酸化ニッケル電極は、表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されたニッケルが 2 価以下の価数を有する水酸化ニッケル粉末と、表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されたニッケルが 2 価を超える価数を有する水酸化ニッケル粉末とが混合されて三次元多孔体に保持されているものが好ましく、さらに、混合されて三次元多孔体に保持される水酸化ニッケル粉末全体のニッケル平均価数が、2.07 価以上の価数を有しているものが特に好ましい。

【0015】2 価を超える価数を有する水酸化ニッケルによる導電性向上の効果は、これを含む水酸化ニッケル活物質全体のニッケルの平均価数が 2.07 価を超えない場合は効果が小さいためである。

【0016】そして、本発明の水酸化ニッケル電極においても、上記水酸化ニッケル電極に含有されるニッケルが 2 価を超える価数を有する水酸化ニッケル粉末のニッケルの平均価数が、これを被覆する 2 価を超える価数を有するコバルト化合物のコバルトの平均価数を超えないようなものとなっているのがより好ましい。

【0017】

【発明の実施の形態】本発明粉末の主成分である水酸化ニッケル粉末は、ニッケルの価数が 2 価を超えるものであるために、従来の水酸化ニッケル粉末よりも導電性に優れ、なおかつ水酸化ニッケル粉末の表面に形成されたコバルトの価数が 2 価を超えるコバルト化合物層も高導電性を示すことから、水酸化ニッケル電極に使用することで、高い導電性を示す水酸化ニッケル電極を製作することができ、それによりアルカリ電池の水酸化ニッケル電極の利用率を向上させることができるものである。

【0018】本発明のアルカリ電池用水酸化ニッケル粉末は、アルカリ電池、特にアルカリ蓄電池の正極活物質として用いられ、これを単独で活物質として用いても良いし、予め水酸化ニッケル粒子表面にオキシ水酸化コバルトを形成して製造されるような水酸化ニッケルを主体とする粉末であって、該水酸化ニッケル粉末の表面にコバルトの価数が 2 価を超えるコバルト化合物が形成された活物質と混合して用いても良い。さらに、他の活物質や添加物が混合されても良い。特に、上記のように、表面にコバルトの価数が 2 価を超えるコバルト化合物が形成されたニッケルが 2 価以下の価数を有する水酸化ニッケル粉末を混合して用いる場合は、正極内の水酸化ニッケル活物質の Ni 価数の制御を行い易いというメリットがあるので良い。

【0019】そして、本発明の活物質は、電極作製時の

原料として用いられて、好ましくは三次元多孔体支持体に保持され、電極とされる。

【0020】

【実施例】以下、実施例および比較例を用いて本発明についてさらに具体的に説明する。

（実施例1）水酸化ニッケル粉末を重量比で約3倍の精製水中に分散し、23wt%の水酸化ナトリウム水溶液を用いてpH11の弱アルカリ性に調整した。この分散液を攪拌しながら、不活性ガス雰囲気下で硫酸コバルト水溶液を滴下させて水酸化ニッケル粉末の表層に水酸化ニッケルに対して10wt%の水酸化コバルトで被覆された水酸化ニッケル活物質を製作した。続いて、この活物質を含むアルカリ性懸濁液を空気中に取り出し、これを80℃に加熱しながら3時間攪拌した後、洗浄・乾燥*



本活物質粉末Aについて、化学分析をおこなったところ、コバルトの価数は3.0価、ニッケルの価数は2.5価であった。また、本活物質粉末AについてX線回折分析をおこなったところ、オキシ水酸化コバルト、水酸化ニッケルおよびオキシ水酸化ニッケルの回折ピークが確認された。

【0023】上記のようにして得られた活物質粉末A100重量部とカルボキシメチルセルロース1重量部と精製水を用いてスラリー状試料を製作し、これを発泡ニッケル基体中含浸・プレスした後、乾燥して、本発明の活物質粉末Aを使用した水酸化ニッケル電極Aを得た。負極は、酸化カドミウム粉末70重量部と金属カドミウム粉末30重量部を主成分とするスラリー状試料をパンチングメタル上に塗布し、乾燥後、プレスして公知のカドミウム負極板を製作した。以上で製作した正極板3枚と負極板4枚と親水性を付与したポリオレフィン製セパレータとを用いてエレメントを形成し、水酸化カリウム水溶液を主成分とする電解液を注入した電池缶内に挿入し、安全弁を内蔵した蓋部分と電池缶を溶接して本発明活物質粉末Aを使用した本発明電池Aを得た。

（比較例1）本発明活物質粉末Aの前駆体として得られた、オキシ水酸化コバルトで被覆された水酸化ニッケル100重量部とカルボキシメチルセルロース1重量部と精製水を用いてスラリー状試料を製作し、これを発泡ニッケル基体中含浸・プレスした後、乾燥して水酸化ニッケル電極Bを製作した。この水酸化ニッケル電極Bを用いたこと以外は、実施例と同様にして比較電池Bを得た。

（比較例2）水酸化ニッケル粉末200g（約2.16mol）を5wt%水酸化ナトリウム水溶液2L中に分散し、反応式（1）にしたがって、攪拌しながら酸化剤であるペルオキシ二硫酸ナトリウム309g（約1.30mol）を加えて反応させた。10時間攪拌後、洗浄・乾燥して活物質粉末Cを得た。

【0024】本活物質粉末Cは、化学分析の結果、ニッ

*して2価を越えるコバルト化合物で被覆された水酸化ニッケルを得た。この試料について化学分析をおこなったところ、コバルト化合物被覆層はコバルトの価数が3.0価のオキシ水酸化コバルトであり、水酸化ニッケルのニッケルの価数は2.0価であることがわかった。

【0021】上記オキシ水酸化コバルトで被覆された水酸化ニッケル330g（水酸化ニッケル約3.24mol）を室温で5wt%水酸化ナトリウム水溶液5L中に分散し、反応式（1）にしたがって、攪拌しながら酸化剤であるペルオキシ二硫酸ナトリウム231g（約0.98mol）を加えて反応させた。10時間攪拌後、洗浄・乾燥して活物質粉末Aを得た。

【0022】

ケルの価数は3.0であり、X線回折分析の結果から、β-オキシ水酸化ニッケルであることが確認された。

【0025】上記のようにして得られた活物質粉末Cと、10wt%オキシ水酸化コバルトで被覆された水酸化ニッケル粉末とを45:50（重量比）の割合で乾式混合し、この混合粉末100重量部とカルボキシメチルセルロース1重量部と精製水を用いてスラリー状試料を製作し、これを発泡ニッケル基体中含浸・プレスした後、乾燥して、活物質粉末Cを使用した水酸化ニッケル電極Cを得た。この水酸化ニッケル電極Cを用いたこと以外は、実施例と同様にして比較電池Cを得た。これらの電池は正極の理論容量がすべて1000mAhであり、充電・放電ともに正極が容量制限極となるよう、負極の容量を過剰にして製作したものである。

【0026】以上の電池は、25℃で100mAで12時間充電し、100mAで0.8Vまで放電するという充放電サイクルを10回繰り返した後、以下の条件で放電容量を測定した。

- ・ 充電……200mAで120%（6時間）
- ・ 放電……200mAで0.8Vまで
- ・ 温度……25℃

試験結果を図1に示す。オキシ水酸化コバルトで被覆された水酸化ニッケルを用いた比較電池Bの放電容量が約980mAh、オキシ水酸化ニッケル粉末とオキシ水酸化コバルトで被覆された水酸化ニッケル粉末とを用いた比較電池Cの放電容量が約1000mAhであったのに対し、オキシ水酸化コバルトで被覆されたニッケルの価数が2.5価の水酸化ニッケルを主体とする活物質を用いた本発明電池Aの放電容量は、約1030mAhと大きい値を示した。

【0027】正極中にオキシ水酸化ニッケルが含まれる電池AおよびCは、オキシ水酸化ニッケルを含まない比較電池Bよりも放電容量が大きかった。これは正極中にオキシ水酸化ニッケルが含まれることで活物質自体の導電性が高くなり、活物質の利用率が向上したものと考え

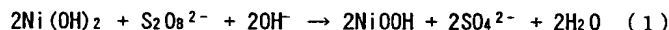
られる。

【0028】また、オキシ水酸化ニッケルと、オキシ水酸化コバルトで被覆された水酸化ニッケルを用いた比較電池Cよりも、オキシ水酸化コバルトで被覆されたニッケルの価数が2.5価の水酸化ニッケルを主体とする活物質を用いた本発明電池Aの放電容量が大きいのは、本発明電池Aでは水酸化ニッケル表面が、放電末期においても導電性を維持できるオキシ水酸化コバルトにより均一に被覆されたためであると推察される。

【0029】本実施例においては、負極にカドミウム電極を用いたニッケル-カドミウム蓄電池を例に挙げて説明したが、負極に亜鉛電極や水素吸蔵電極などを用いた他のアルカリ蓄電池であっても、同様の効果が得られる。

【0030】また、本発明の水酸化ニッケル活物質は、ニッケル化合物のみからなる単一組成の粒子のほかに、コバルト、マンガン、亜鉛、カドミウム、カルシウムから選ばれた少なくとも1種の元素が固溶した場合であっても、同様の効果が得られるものである。

(実施例2) 水酸化ニッケル粉末を重量比で約3倍の精製水中に分散し、23wt%の水酸化ナトリウム水溶液を用いてpH11の弱アルカリ性に調整した。この分散液を攪拌しながら、不活性ガス雰囲気下で硫酸コバルト水溶液を滴下させて水酸化ニッケル粉末の表層に水酸化ニッケルに対して10wt%の水酸化コバルトで被覆さ*



前記3価コバルト化合物で被覆された水酸化ニッケル粉末85重量部と、3価コバルト化合物で被覆されたオキシ水酸化ニッケル粉末15重量部と、カルボキシメチルセルロース粉末2重量部を精製水に加えて製作したスラリー状試料を発泡ニッケル基板中に含浸・プレスした後、乾燥して、本発明による水酸化ニッケル電極Dを得た。ここで、この水酸化ニッケル電極Dのニッケルの平均価数を調査したところ、その価数は2.15価であることが明らかとなった。負極は、公知のAB5型水素吸蔵合金を主成分とするスラリー状試料をパンチングメタル上に塗布し、乾燥後、プレスして製作した。以上で製作した正極板3枚と負極板4枚と親水性を付与したポリオレフィン製セパレータとを用いてエレメントを形成し、水酸化カリウム水溶液を主成分とする電解液を注入した電池缶内に挿入し、安全弁を内蔵した蓋部分と電池缶を溶接して本発明電池Dを得た。

(比較例3) 水酸化ニッケル粉末を重量比で約3倍の精製水中に分散し、23wt%の水酸化ナトリウム水溶液を用いてpH11の弱アルカリ性に調整した。この分散液を攪拌しながら、不活性ガス雰囲気下で硫酸コバルト水溶液を滴下させて水酸化ニッケル粉末の表層に水酸化ニッケルに対して11.3wt%の水酸化コバルトで被覆された水酸化ニッケル活物質を製作した。続いて、この活物質を含むアルカリ性懸濁液を空気中に取り出し、

*れた水酸化ニッケル活物質を製作した。続いて、この活物質を含むアルカリ性懸濁液を空気中に取り出し、これを80℃に加熱しながら3時間攪拌した後、洗浄・乾燥して2価を超えるコバルト化合物で被覆された水酸化ニッケルを得た。この試料について化学分析をおこなったところ、コバルト化合物被覆層はコバルトの価数が3.0価のオキシ水酸化コバルトであり、水酸化ニッケルのニッケルの価数は2.0価であることがわかった。つぎに、以下の化学反応式(1)に従って、前記2価を超えるコバルト化合物で被覆された水酸化ニッケル粉末に対して重量比で約20倍の26wt%水酸化カリウム水溶液中に、2価を超えるコバルト化合物で被覆された水酸化ニッケル粉末とペルオキシ二硫酸カリウム粉末をモル比2:1.4の割合で分散させ、室温で10時間攪拌した。反応後、分散溶液をろ過して得られた黑色粉末を、洗浄液のpHが7になるまで精製水で洗浄・乾燥して、2価を超えるコバルト化合物で被覆されたオキシ水酸化ニッケル粉末を得た。これについても、先と同様の化学分析をおこなったところ、ニッケル・コバルトともに3.0価を示すことが確認された。本実施例ではコバルト被覆層の価数が酸化処理以前から3価を示すものであるので、ペルオキシ二硫酸カリウムによる酸化を受けなかったものと考えられる。

【0031】

これを80℃に加熱しながら3時間攪拌した後、洗浄・乾燥して2価を超えるコバルト化合物で被覆された水酸化ニッケルを得た。この試料について化学分析をおこなったところ、コバルト化合物被覆層はコバルトの価数が3.0価のオキシ水酸化コバルトであり、水酸化ニッケルのニッケルの価数は2.0価であることがわかった。

【0032】この2価を超えるコバルト化合物で被覆された水酸化ニッケル粉末88.5重量部と、オキシ水酸化ニッケル粉末11.5重量部とを用いたこと以外は、実施例の水酸化ニッケル電極Dと同様にして水酸化ニッケル電極Eを製作し、さらに比較電池Eを得た。なお、水酸化ニッケル電極Eのニッケルの平均価数を調査したところ、その価数は2.15価であることが明らかとなった。

(比較例4) 水酸化コバルト粉末10重量部と、水酸化ニッケル粉末90重量部と、カルボキシメチルセルロース粉末2重量部を精製水に加えて製作したスラリー状試料を、発泡ニッケル基板中に含浸・プレスした後、乾燥して、水酸化ニッケル電極Fを製作した。その他は実施例と同様にして比較電池Fを得た。なお、水酸化ニッケル電極Fのニッケルの平均価数を調査したところ、その価数は2.00価であることが明らかとなった。これらの電池は、正極の理論容量がすべて1000mAhである。以上の電池を、室温中で100mAで12時間充電

後、100mAで0.8Vまで放電するという充放電サイクルを10回繰り返して、水素吸蔵合金負極を充分活性化した後、以下の条件で放電容量を測定した。

- ・充電……200mAで120% (6時間)
- ・放電……200mAで0.8Vまで

温度……25℃

試験結果を図2に示す。2価を超えるコバルト化合物で被覆された水酸化ニッケル粉末と、オキシ水酸化ニッケル粉末を活性物質とした比較電池Eの放電容量が約1000mAh、水酸化ニッケル粉末と水酸化コバルト粉末を含有した比較電池Fの放電容量が約960mAhであったのに対し、2価を超えるコバルト化合物で被覆された水酸化ニッケル粉末と2価を超えるコバルト化合物で被覆されたオキシ水酸化ニッケル粉末を含有した本発明電池Dの放電容量は約1030mAhと大きい値を示した。

【0033】比較電池Fの放電容量よりも本発明電池Dの放電容量の方が大きい原因としては、比較電池Fでは、導電剤のオキシ水酸化コバルトの元原料として添加した水酸化コバルトが単に粉末として混合されていたのに対し、本発明電池Dでは、高い導電性を有するオキシ水酸化コバルトが水酸化ニッケル粉末およびオキシ水酸化ニッケル粉末の表面に被覆されていたこと、また水酸化ニッケルよりも導電性の高いオキシ水酸化ニッケルが極板内に存在するためであると考えられる。また、比較電池Eに添加したオキシ水酸化ニッケル粉末の近傍には、放電末期の導電性を維持する導電剤（オキシ水酸化コバルト）が少なく、そのため、本発明電池よりも放電

容量が小さかったものと考えられる。このようにして、本発明電池Dは、その充放電過程のどの状態においても高い導電性を維持することができ、その結果として高い活物質利用率を発現できるものである。なお、水酸化ニッケル粉末や2価を超える価数の水酸化ニッケル粉末中に、少量の亜鉛やコバルトやカドミウム等の水酸化物が含まれた場合であっても、本発明電極の特性を低下させるものではない。2価を超える価数の水酸化ニッケル粉末製作のための水酸化ニッケル粉末の酸化や、2価を超えるコバルト化合物を得る方法は、電気化学的手法あるいは化学的手法のいずれでもよい。また、あらかじめ酸化状態の高い水酸化ニッケルを主体とする活物質、および水酸化ニッケルを主体とする活物質それぞれの表層に被覆されたオキシ水酸化コバルトをアルカリ蓄電池製作前の水酸化ニッケル電極に適用することにより、放電できない負極活物質の量を減少させることができ、アルカリ蓄電池の高エネルギー密度化をも実現できると考えられる。

【0034】

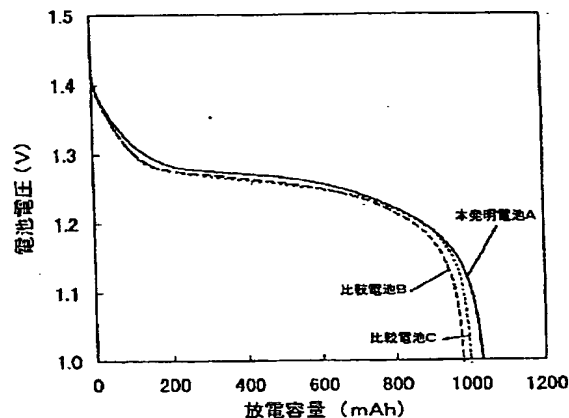
【発明の効果】本発明によれば、水酸化ニッケル電極の活物質利用率を向上させ、アルカリ電池のさらなる高容量化が可能となる。

【図面の簡単な説明】

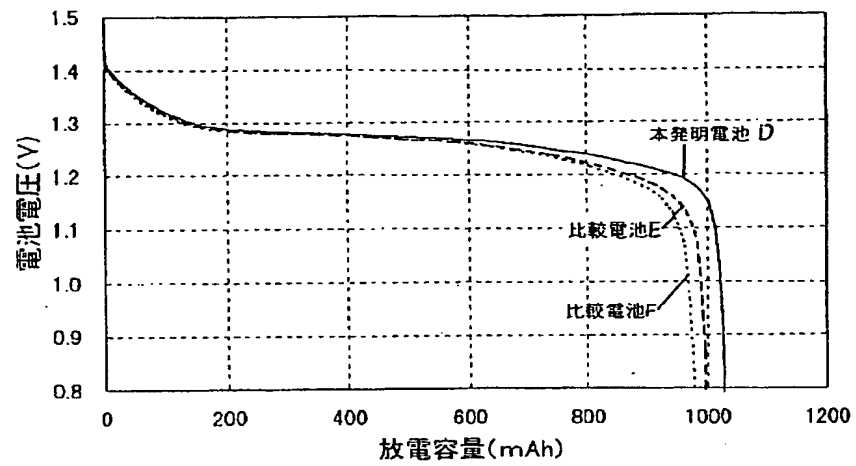
【図1】本発明に係るニッケル-カドミウム電池の放電特性を示した図。

【図2】本発明に係るニッケル-金属水素化物電池の放電特性を示した図。

【図1】



【図 2】



フロントページの続き

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CLAIMS

[Claim(s)]

[Claim 1] the alkaline cell which the valence of nickel is the powder which makes the nickel hydroxide exceeding divalent a subject, and is characterized by forming in the front face of this nickel hydroxide powder the cobalt compound to which the valence of cobalt exceeds divalent -- service water -- nickel oxide powder

[Claim 2] Nickel hydroxide powder for alkaline cells according to claim 1 characterized by not exceeding the average valence of the cobalt of the cobalt compound which has the valence to which the average valence of the nickel of the above-mentioned nickel hydroxide powder exceeds divalent [which covers this].

[Claim 3] The nickel hydroxide electrode which it is the nickel hydroxide electrode which comes to hold the powder which makes nickel hydroxide a subject to a three-dimensions porous body, and the powder which makes the aforementioned nickel hydroxide a subject is powder which makes a subject the nickel hydroxide to which the valence of nickel exceeds divalent, and is characterized by forming in the front face of this nickel hydroxide powder the cobalt compound to which the valence of cobalt exceeds divalent.

[Claim 4] The nickel hydroxide electrode to which the nickel average valence of the whole nickel hydroxide powder which is characterized by mixing the nickel hydroxide powder characterized by providing the following, and being held at the three-dimensions porous body, and is held at a three-dimensions porous body is characterized by having the valence of 2.07 or more **. Nickel hydroxide powder with which the nickel with which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face has a valence below divalent. The valence to which the nickel with which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face exceeds divalent.

[Claim 5] The nickel hydroxide electrode according to claim 2 or 3 characterized by not exceeding the average valence of the cobalt of the cobalt compound which has the valence to which the average valence of the nickel of the nickel hydroxide powder which has the valence to which the nickel contained in the above-mentioned nickel hydroxide electrode exceeds divalent exceeds divalent [which covers this].

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nickel hydroxide electrode which used the nickel hydroxide active material for alkaline cells, and this.

[0002]

[Description of the Prior Art] The nickel hydroxide electrode which makes an active material the compound which makes nickel hydroxide a subject is used as a positive electrode of alkaline cells, such as a Ni-Cd battery and a nickel-metal-hydride battery. Since it is used as a power supply of small pocket electronic equipment and high capacity-ization of an alkaline battery is called for as a means of the improvement in functional, these alkaline batteries have the indispensable formation of high-energy density of the nickel hydroxide electrode which determines the service capacity of an alkaline battery.

[0003] Conventionally, many things of the sintering formula which a nickel hydroxide active material is infiltrated on the substrate which was made to sinter nickel powder on a porous punching metal, and was obtained as a nickel hydroxide electrode, and is manufactured have been used. However, the sintering formula nickel hydroxide electrode had the porosity of a substrate in general as small as 80%, and since it was difficult to be filled up with a lot of active materials, it was disadvantageous for the formation of high-energy density of a nickel hydroxide electrode.

[0004] The nickel hydroxide electrode of non-sintering which, on the other hand, made the nickel hydroxide active material hold to this using the letter nickel of foaming and fibrous nickel which are a three-dimensions metal porous body as a substrate has the porosity of a substrate as high as 95% or more, and it is advantageous to the formation of high-energy density of a nickel hydroxide electrode as compared with the aforementioned sintering formula nickel hydroxide electrode. From this, research on high-capacity-izing of the latest alkaline battery is mainly performed using the non-sintering nickel hydroxide electrode. In this non-sintering nickel hydroxide electrode, it is necessary for a low reason, for the conductivity of nickel hydroxide to mix cobalt-compound metallurgy group cobalt, such as cobalt hydroxide, 1 cobalt oxide, and cobalt sub oxide, in a nickel hydroxide electrode as an electric conduction agent, or to add by the method of covering a nickel hydroxide particle front face with these as indicated by JP,62-117267,A.

[0005] These added cobalt compounds are changed into conductive high oxy-cobalt hydroxide by electrochemical oxidization in the Chemicals initial charge, form a conductive network in an electrode, and are considered to act as an effective electric conduction agent in a nickel hydroxide electrode. In addition, according to the method of covering a nickel hydroxide particle front face, rather than the case where a cobalt compound is added independently, the touch area of a cobalt compound and nickel hydroxide is large, and the effect of improvement in an active material utilization factor becomes large.

[0006]

[Problem(s) to be Solved by the Invention] Although the nickel hydroxide which is the active material of the nickel hydroxide electrode of an alkaline battery oxidizes by charge, and turns into oxy-nickel hydroxide and it is returned to nickel hydroxide by electric discharge, the conductivity of this nickel hydroxide is the low matter from oxy-nickel hydroxide. For this reason, there is a problem of a low in especially the charging efficiency of the Chemicals initial charge in early stages of charge.

[0007] Then, how to add uniformly beforehand the oxy-nickel hydroxide which is the matter with conductivity higher than nickel hydroxide at the time of manufacture of a nickel hydroxide electrode is considered as it is indicated by JP,2-262245,A and JP,2-234356,A in order to solve such a problem for example. However, when the valence of cobalt, such as the above-mentioned conventional cobalt hydroxide and 1 cobalt oxide, added oxy-nickel hydroxide in the nickel hydroxide electrode which added the cobalt-compound metallurgy group cobalt below divalent, compared with the service capacity computed by calculation, the capacity is small and the bird clapper was found.

[0008] Then, or a part, even if [whose valence of cobalt is a cobalt compound below divalent as a result of studying this cause] the valence of cobalt exceeds divalent, this invention persons The valence of cobalt to a low case rather

than the nickel hydroxide of the valence exceeding divalent a part of this cobalt compound Oxidize by the high oxy-nickel hydroxide of oxidizing power, and it becomes a high order cobalt compound. The conclusion that formation of the conductive network of the oxy-cobalt hydroxide considered to be required in order for the maldistribution of a cobalt compound to arise in a nickel hydroxide electrode and to maintain the conductivity of a nickel hydroxide electrode is no longer performed fully is reached. It made it possible to solve this problem by forming oxy-cobalt hydroxide in the nickel hydroxide particle front face beforehand based on this. And this invention persons found out the method of enlarging service capacity further in this process. this invention -- this alkaline cell improved further -- service water -- it aims at offering a nickel oxide active material and the nickel hydroxide electrode using this [0009]

[Means for Solving the Problem] The valence of nickel is the powder which makes the nickel hydroxide exceeding divalent a subject, and the nickel hydroxide powder for alkaline cells of this invention is characterized by forming in the front face of this nickel hydroxide powder the cobalt compound to which the valence of cobalt exceeds divalent.

[0010] Moreover, the nickel hydroxide electrode of this invention is a nickel hydroxide electrode which comes to hold the powder which makes nickel hydroxide a subject to a three-dimensions porous body, and the powder which makes the aforementioned nickel hydroxide a subject is powder which makes a subject the nickel hydroxide to which the valence of nickel exceeds divalent, and it is characterized by forming in the front face of this nickel hydroxide powder the cobalt compound to which the valence of cobalt exceeds divalent.

[0011] Although the nickel hydroxide powder of this invention makes a subject the nickel hydroxide to which the valence of nickel exceeds divalent, if the valence exceeds trivalent, in order that the gamma-oxy-nickel hydroxide considered to be ***** may generate a bad influence for the charge-and-discharge cycle-life performance of an alkaline battery, as for the valence of the nickel of nickel hydroxide used as the above-mentioned subject, it is desirable that it is below trivalent.

[0012] Moreover, the cobalt compound formed in the front face of the nickel hydroxide powder with which the valence of nickel exceeds divalent It is good to be formed so that nickel hydroxide powder may be covered in layers more preferably. the valence of the cobalt Since it becomes difficult for a cobalt compound to tend to oxidize for the strong oxidizing power of the above-mentioned nickel hydroxide powder, and to maintain the conductivity a low case, it is more more desirable than the valence of the nickel of nickel hydroxide powder that they are the valence of nickel hydroxide powder, equivalent, or more than it. That is, although the conductivity of the nickel hydroxide powder used as an active material is borne, the number of these cobalt compounds is one, and it is good to make it not exceed the average valence of the cobalt of the cobalt compound which has high conductivity and has the valence to which the average valence of the nickel of nickel hydroxide powder exceeds divalent [which covers this].

[0013] Moreover, as for the above-mentioned three-dimensions porous body, it is desirable that they are three-dimensions metal porous bodies, such as letter nickel of foaming and fibrous nickel.

[0014] Furthermore, the nickel hydroxide powder with which, as for the nickel hydroxide electrode of this invention, the nickel with which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face has a valence below divalent, What the nickel hydroxide powder which has the valence to which the nickel with which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face exceeds divalent is mixed, and is held at the three-dimensions porous body is desirable. Furthermore, especially the thing in which the nickel average valence of the whole nickel hydroxide powder which is mixed and is held at a three-dimensions porous body has the valence of 2.07 or more **s is desirable.

[0015] the effect of the conductive improvement by the nickel hydroxide which has a valence exceeding divalent has a small effect, when the average valence of the nickel of the whole nickel hydroxide active material containing this does not exceed 2.07 ** -- it is a sake

[0016] And it is more desirable that it is what does not exceed the average valence of the cobalt of the cobalt compound which has the valence to which the average valence of the nickel of the nickel hydroxide powder which has the valence to which the nickel contained in the above-mentioned nickel hydroxide electrode exceeds divalent also in the nickel hydroxide electrode of this invention exceeds divalent [which covers this].

[0017]

[Embodiments of the Invention] The nickel hydroxide powder which is the principal component of this invention powder Since the valence of nickel is a thing exceeding divalent, the conventional nickel hydroxide powder is excelled in conductivity. In addition, since the cobalt-compound layer in which the valence of the cobalt formed in the front face of nickel hydroxide powder exceeds divalent also shows high conductivity, by and the thing to use for a nickel hydroxide electrode The nickel hydroxide electrode which shows high conductivity can be manufactured, and, thereby, the utilization factor of the nickel hydroxide electrode of an alkaline cell can be raised.

[0018] The nickel hydroxide powder for alkaline cells of this invention is used as a positive active material of an alkaline cell, especially an alkaline battery, and this may be independently used for it as an active material, and it is the

powder which makes a subject nickel hydroxide which forms oxy-cobalt hydroxide in a nickel hydroxide particle front face beforehand, and is manufactured, and it may mix with the active material by which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face of this nickel hydroxide powder, and it may be used for it. Furthermore, other active materials and additives may be mixed. Since there is a merit of being easy to control nickel valence of the nickel hydroxide active material in a positive electrode especially when the nickel with which the cobalt compound to which the valence of cobalt exceeds divalent was formed in the front face as mentioned above mixes and uses the nickel hydroxide powder which has a valence below divalent, it is good.

[0019] And the active material of this invention is used as a raw material at the time of electrode production, is held preferably at a three-dimensions porous-body base material, and let it be an electrode.

[0020]

[Example] Hereafter, this invention is explained still more concretely using an example and the example of comparison.

(Example 1) It distributed in the about 3 times as many purified water as this by the weight ratio, and nickel hydroxide powder was adjusted to the weak alkalinity of pH 11 using 23wt% sodium-hydroxide solution. The nickel hydroxide active material which was made to trickle cobalt-sulfate solution under inert gas atmosphere, and was covered with 10wt(s)% cobalt hydroxide by the surface of nickel hydroxide powder to nickel hydroxide was manufactured stirring these dispersion liquid. Then, the alkaline suspension containing this active material was taken out in air, and after stirring for 3 hours, heating this at 80 degrees C, the nickel hydroxide covered with the cobalt compound which washes and dries and exceeds divalent was obtained. When the chemical analysis was performed about this sample, the valence of cobalt of a cobalt-compound enveloping layer is oxy-cobalt hydroxide of 3.0 **, and it turns out that the valence of the nickel of nickel hydroxide is 2.0 **.

[0021] 330g (about 3.24 mols of nickel hydroxide) of nickel hydroxide covered with the above-mentioned oxy-cobalt hydroxide -- a room temperature -- 5wt(s)% -- it distributes in sodium-hydroxide solution 5L, and stirring, peroxydisulfuric-acid sodium 231g (about 0.98 mols) which is an oxidizer was added, and was made to react according to a reaction formula (1) After 10-hour stirring, it washed and dried and the active material powder A was obtained.

[0022]

$$2\text{nickel}(\text{OH})_2 + \text{S}_2\text{O}_8^{2-} + 2\text{OH}^- \rightarrow 2\text{NiOOH} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \dots (1)$$

When the chemical analysis was performed about this active material powder A, the valence of 3.0 ** and nickel of the valence of cobalt was 2.5 **. Moreover, when analyzed by X-ray diffraction about this active material powder A, the diffraction peak of oxy-cobalt hydroxide, nickel hydroxide, and oxy-nickel hydroxide was checked.

[0023] After manufacturing the slurry-like sample using the active material powder A 100 weight section and the carboxymethyl-cellulose 1 weight section which were obtained as mentioned above, and the purified water and sinking in and pressing this at a foaming nickel base, it dried and the nickel hydroxide electrode A which used the active material powder A of this invention was obtained. The negative electrode applied the slurry-like sample which makes a principal component the cadmium-oxide powder 70 weight section and the metal cadmium powder 30 weight section on the punching metal, after dryness, was pressed and manufactured the well-known cadmium negative-electrode board. The element was formed using three positive-electrode boards and four negative-electrode boards which were manufactured above, and the separator made from a polyolefine which gave the hydrophilic property, it inserted into the cell can which poured in the electrolytic solution which makes potassium-hydroxide solution a principal component, and this invention cell A which welded a part for a covering device and the cell can which contained the relief valve, and used this invention active material powder A was obtained. (Example 1 of comparison) After manufacturing the slurry-like sample using the nickel hydroxide 100 weight section, the carboxymethyl-cellulose 1 weight section, and the purified water which were obtained as a precursor of this invention active material powder A and which were covered with oxy-cobalt hydroxide and sinking in and pressing this at a foaming nickel base, it dried and the nickel hydroxide electrode B was manufactured. The comparison cell B was obtained like the example except having used this nickel hydroxide electrode B. (Example 2 of comparison) 200g (about 2.16 mols) of nickel hydroxide powder -- 5wt(s)% -- it distributes in sodium-hydroxide solution 2L, and stirring, peroxydisulfuric-acid sodium 309g (about 1.30 mols) which is an oxidizer was added, and was made to react according to a reaction formula (1) After 10-hour stirring, it washed and dried and the active material powder C was obtained.

[0024] It was checked that the valence of nickel is 3.0 and this active material powder C is the beta-oxy-nickel hydroxide from the result of X-ray diffraction analysis as a result of a chemical analysis.

[0025] After having blended dryly the active material powder C obtained as mentioned above and the nickel hydroxide powder covered with 10wt% oxy-cobalt hydroxide at a rate of 45:50 (weight ratio), manufacturing the slurry-like sample in this end of mixed powder using the 100 weight sections, the carboxymethyl-cellulose 1 weight section, and the purified water and sinking in and pressing this at a foaming nickel base, it dried and the nickel hydroxide electrode C which used the active material powder C was obtained. The comparison cell C was obtained like the example except

having used this nickel hydroxide electrode C. All the geometric capacity of a positive electrode is 1000mAh(s), capacity of a negative electrode is made superfluous and, as for these cells, a positive electrode manufactures charge and electric discharge so that it may become a capacity limit pole.

[0026] It charged by 100mA at 25 degrees C for 12 hours, and the above cell measured service capacity on condition that the following, after repeating the charge-and-discharge cycle of discharging to 0.8V by 100mA, 10 times.

- Charge It is 200mA and is 120% (6 hours).

- Electric discharge It is - to 0.8V at 200mA. Temperature .. 25-degree-C test result is shown in drawing 1 . The service capacity of the comparison cell B using the nickel hydroxide covered with oxy-cobalt hydroxide showed the value with the as large service capacity of this invention cell A using the active material to which the valence of the nickel covered with oxy-cobalt hydroxide makes the nickel hydroxide of 2.5 ** a subject as about 1030 mAh(s) to the service capacity of the comparison cell C using about 980 mAh(s), oxy-nickel hydroxide powder, and the nickel hydroxide powder covered with oxy-cobalt hydroxide having been about 1000 mAh(s).

[0027] The cells A and C by which oxy-nickel hydroxide is contained all over a positive electrode had service capacity larger than the comparison cell B which does not contain oxy-nickel hydroxide. The conductivity of the active material itself becomes high by oxy-nickel hydroxide being contained all over a positive electrode, and this is considered that the utilization factor of an active material improved.

[0028] Moreover, the thing with the larger service capacity of this invention cell A using the active material to which the valence of the nickel covered with oxy-cobalt hydroxide makes the nickel hydroxide of 2.5 ** a subject than the comparison cell C using oxy-nickel hydroxide and the nickel hydroxide covered with oxy-cobalt hydroxide is imagined to be because for the nickel hydroxide front face to have been uniformly covered with the oxy-cobalt hydroxide which can maintain conductivity also in the electric discharge last stage by this invention cell A.

[0029] In this example, although the Ni-Cd battery which used the cadmium electrode for the negative electrode was mentioned as the example and explained, even if it is other alkaline batteries which used the zinc electrode, the metal hydride electrode, etc. for the negative electrode, the same effect is acquired.

[0030] Moreover, the same effect is acquired even if the nickel hydroxide active material of this invention is the case where at least one sort of elements chosen from cobalt, manganese, zinc, cadmium, and calcium dissolve besides the particle of the single composition which consists only of a nickel compound.

(Example 2) It distributed in the about 3 times as many purified water as this by the weight ratio, and nickel hydroxide powder was adjusted to the weak alkalinity of pH 11 using 23wt% sodium-hydroxide solution. The nickel hydroxide active material which was made to trickle cobalt-sulfate solution under inert gas atmosphere, and was covered with 10wt(s)% cobalt hydroxide by the surface of nickel hydroxide powder to nickel hydroxide was manufactured stirring these dispersion liquid. Then, the alkaline suspension containing this active material was taken out in air, and after stirring for 3 hours, heating this at 80 degrees C, the nickel hydroxide covered with the cobalt compound which washes and dries and exceeds divalent was obtained. When the chemical analysis was performed about this sample, the valence of cobalt of a cobalt-compound enveloping layer is oxy-cobalt hydroxide of 3.0 **, and it turns out that the valence of the nickel of nickel hydroxide is 2.0 **. the nickel hydroxide powder covered with the cobalt compound exceeding the aforementioned divalent one next according to the following reaction formulas (1) -- receiving -- a weight ratio -- about 20 times many 26wt(s)[as this] % -- a mole ratio 2:1.4 comes out of the nickel hydroxide powder and potassium-peroxodisulfate powder which were covered with the cobalt compound exceeding divalent comparatively into potassium-hydroxide solution, and it was made to distribute, and stirred at the room temperature for 10 hours After the reaction, the black powder which filtered the distributed solution and was obtained was washed and dried by the purified water until pH of a penetrant remover was set to 7, and the oxy-nickel hydroxide powder covered with the cobalt compound exceeding divalent was obtained. When the same chemical analysis as the point was performed also with this, it was checked that nickel cobalt shows 3.0 **. By this example, since the valence of a cobalt enveloping layer shows trivalent from oxidation treatment or before, it is thought that oxidization by the potassium peroxodisulfate was not received.

[0031]

$$2\text{Ni}(\text{OH})_2 + \text{S}_2\text{O}_8^{2-} + 2\text{OH}^- \rightarrow 2\text{NiOOH} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (1)$$

After sinking in and pressing the slurry-like sample which added the nickel hydroxide powder 85 weight section covered with the aforementioned trivalent cobalt compound, the oxy-nickel hydroxide powder 15 weight section covered with the trivalent cobalt compound, and the carboxymethyl-cellulose powder 2 weight section to the purified water, and manufactured them in a foaming nickel substrate, it dried and the nickel hydroxide electrode D by this invention was obtained. Here, when the average valence of the nickel of this nickel hydroxide electrode D was investigated, the valence became clear [that they are 2.15 **]. The negative electrode applied on the punching metal, and the slurry-like sample which makes a principal component well-known AB5 type hydrogen storing metal alloy was pressed after dryness, and it manufactured it. The element was formed using three positive-electrode boards and four

negative-electrode boards which were manufactured above, and the separator made from a polyolefine which gave the hydrophilic property, it inserted into the cell can which poured in the electrolytic solution which makes potassium-hydroxide solution a principal component, a part for a covering device and the cell can which contained the relief valve were welded, and this invention cell D was obtained.

(Example 3 of comparison) It distributed in the about 3 times as many purified water as this by the weight ratio, and nickel hydroxide powder was adjusted to the weak alkalinity of pH 11 using 23wt% sodium-hydroxide solution. The nickel hydroxide active material which was made to trickle cobalt-sulfate solution under inert gas atmosphere, and was covered with 11.3wt(s)% cobalt hydroxide by the surface of nickel hydroxide powder to nickel hydroxide was manufactured stirring these dispersion liquid. Then, the alkaline suspension containing this active material was taken out in air, and after stirring for 3 hours, heating this at 80 degrees C, the nickel hydroxide covered with the cobalt compound which washes and dries and exceeds divalent was obtained. When the chemical analysis was performed about this sample, the valence of cobalt of a cobalt-compound enveloping layer is oxy-cobalt hydroxide of 3.0 **, and it turns out that the valence of the nickel of nickel hydroxide is 2.0 **.

[0032] Except having used the nickel hydroxide powder 88.5 weight section covered with the cobalt compound exceeding divalent [this], and the oxy-nickel hydroxide powder 11.5 weight section, the nickel hydroxide electrode E as well as the nickel hydroxide electrode D of an example was manufactured, and the comparison cell E was obtained further. In addition, when the average valence of the nickel of the nickel hydroxide electrode E was investigated, the valence became clear [that they are 2.15 **].

(Example 4 of comparison) After sinking in and pressing the slurry-like sample which added the cobalt hydroxide powder 10 weight section, the nickel hydroxide powder 90 weight section, and the carboxymethyl-cellulose powder 2 weight section to the purified water, and manufactured them in a foaming nickel substrate, it dried and the nickel hydroxide electrode F was manufactured. Others obtained the comparison cell F like the example. In addition, when the average valence of the nickel of the nickel hydroxide electrode F was investigated, the valence became clear [that they are 2.00 **]. All the geometric capacity of a positive electrode of these cells is 1000mAh(s). After repeating the charge-and-discharge cycle of having discharged after 12-hour charge by 100mA, and discharging the above cell to 0.8V by 100mA in a room temperature, 10 times and activating a hydrogen storing metal alloy negative electrode enough, service capacity was measured on condition that the following.

- Charge It is 200mA and is 120% (6 hours).

- Electric discharge It is temperature to 0.8V at 200mA.. 25-degree-C test result is shown in drawing 2 . The service capacity of the comparison cell E which made the active material the nickel hydroxide powder covered with the cobalt compound exceeding divalent and oxy-nickel hydroxide powder About 1000 mAh(s), As opposed to the service capacity of the comparison cell F containing nickel hydroxide powder and cobalt hydroxide powder having been about 960 mAh(s) The service capacity of this invention cell D containing the nickel hydroxide powder covered with the cobalt compound exceeding divalent and the oxy-nickel hydroxide powder covered with the cobalt compound exceeding divalent showed about 1030 mAh(s) and the large value.

[0033] As a cause that the service capacity of this invention cell D is larger than the service capacity of the comparison cell F As opposed to the cobalt hydroxide added as a former raw material of the oxy-cobalt hydroxide of an electric conduction agent only having been mixed as powder by the comparison cell F by this invention cell D It is thought that it is because conductive high oxy-nickel hydroxide exists in a plate rather than that the oxy-cobalt hydroxide which has high conductivity was covered by the front face of nickel hydroxide powder and oxy-nickel hydroxide powder, and nickel hydroxide. Moreover, near the oxy-nickel hydroxide powder added on the comparison cell E, it is considered what has the service capacity smaller than this invention cell that there are [therefore] few electric conduction agents (oxy-cobalt hydroxide) which maintain the conductivity of the electric discharge last stage. Thus, this invention cell D can maintain high conductivity in every state of the charge-and-discharge process, and can discover an active material utilization factor high as the result. In addition, even if it is the case where hydroxides, such as a small amount of zinc and cobalt, and cadmium, are contained in the nickel hydroxide powder of the valence exceeding nickel hydroxide powder or divalent, the property of this invention electrode is not reduced. Any of the electrochemical technique or the chemical technique are sufficient as oxidization of the nickel hydroxide powder for nickel hydroxide powder manufacture of the valence exceeding divalent, and the method of obtaining the cobalt compound exceeding divalent. Moreover, by applying the oxy-cobalt hydroxide covered by the surface of the active material which makes the high nickel hydroxide of an oxidation state a subject beforehand, and each active material which makes nickel hydroxide a subject to the nickel hydroxide electrode before alkaline battery manufacture, the amount of the negative-electrode active material which cannot discharge can be decreased, and it is thought that high-energy density-ization of an alkaline battery is also realizable.

[0034]

[Effect of the Invention] According to this invention, the active material utilization factor of a nickel hydroxide

electrode is raised, and the further high capacity-ization of an alkaline cell is attained.

[Translation done.]